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Science of the Total Environment 571 (2016) 1358–1369

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Hydrological conditions regulate dissolved organic matter quality in an intermittent headwater stream. From drought to storm analysis

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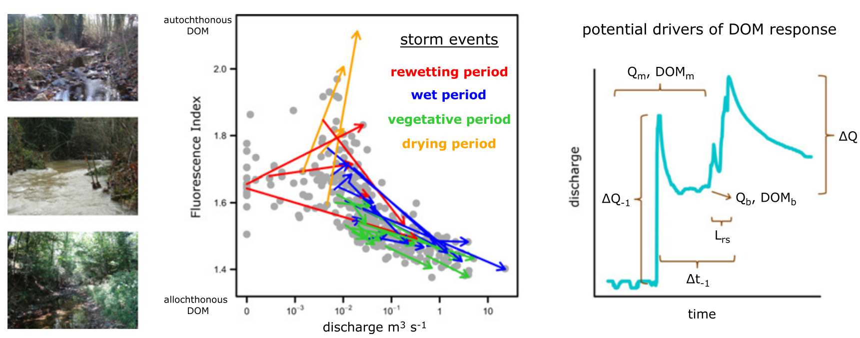
HIGHLIGHTS

- DOM quality in an intermittent stream was assessed using spectroscopic properties.
- High discharge caused the rise of DOM humification and allochthonous character.
- DOM vs. discharge relationship varied across hydrological periods.
- The magnitude of the storm events was the main driver of DOM response.
- DOM quantity, aromaticity and origin were also shaped by the antecedent conditions.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 23 May 2016
Received in revised form 8 July 2016
Accepted 8 July 2016
Available online 25 July 2016

Editor: D. Barcelo

Keywords:
Flood
Water scarcity
Mediterranean stream
Time series
Spectroscopic properties
Hysteresis

ABSTRACT

Storms and droughts are an essential driver for the dissolved organic matter (DOM) concentration in headwater streams. However, the relationship between DOM quality and discharge (Q) has not been addressed in depth and the impact of other hydro-climatic or biogeochemical drivers has not been explored. In this study DOM quality variability was explored at seasonal and storm event scales during an intensive 2.5-year-long sampling in a Mediterranean stream characterized by a severe summer drought. DOM quality was described in terms of absorbance and fluorescence properties. Most of the DOM properties were strongly related to discharge revealing the input of allochthonous, degraded, aromatic, humic and increased-molecular-size DOM under high flow conditions. However, these relationships disappeared or reversed during drying and rewetting periods. Each DOM response at the storm event scale (DOM-Q hysteresis) was outlined with two descriptors that summarised its trend (dilution/flushing/chemostasis) and shape (linear/nonlinear response). Multiple linear regression and commonality analysis showed that, in addition to the magnitude of storm episodes, antecedent hydrological conditions, namely pre-event basal flow and the magnitude of the previous storm event, played a significant role in regulating the trends and shapes of DOM-Q hysteresis.

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1. Introduction

Dissolved organic matter (DOM) plays a key role in freshwater ecosystems: it provides energy and nutrients to heterotrophic bacteria and some algae (Glibert et al., 2001; Wetzel, 1992; Wiegner and Seitzinger, 2001); it attenuates visible and ultraviolet radiation (Blough and Del

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http://dx.doi.org/10.1016/j.scitotenv.2016.07.060
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Vecchio, 2002; Brooks et al., 2005; Foden et al., 2008); it affects the complexation, solubility and mobility of trace metals (Buffle, 1984; Yamashita and Jaffé, 2008); and it takes part in pH regulation (Kerekes et al., 1986). Hydrology is a key driver of the DOM dynamic (Inamdar et al., 2011; von Schiller et al., 2015; Voss et al., 2015). DOM concentration typically increases during high flow conditions in forested streams (Bass et al., 2011; Dhillon and Inamdar, 2014; Hinton et al., 1997; Wiegner et al., 2009). As a result, most organic carbon export occurs during high flows (Raymond and Saiers, 2010). However, long-term studies in boreal streams reported that antecedent hydrological and climatic conditions are also important (Ågren et al., 2010; Raymond and Saiers, 2010; Winterdahl et al., 2011). Consequently, to improve our understanding of the dynamic of DOM during storm events, it would be necessary to take into account the influence of pre-event hydrological conditions.

Most of the studies previously cited focused on the relationship between discharge (Q) and dissolved organic carbon (DOC) concentration. In contrast, little is known about the response of DOM qualitative properties. Spectroscopy techniques based on absorbance and fluorescence are a well-established tool to investigate DOM aromatic content (Fellman et al., 2013), composition (Cawley et al., 2014), origin and freshness (Kolic et al., 2014), degree of humification (He et al., 2013), anthropogenic inputs (Henderson et al., 2009) and potential bioavailability for micro biota (Guillemette and del Giorgio, 2011). Some of these parameters are sensitive to hydrology. Thus, humic-like content, aromaticity, humification degree and DOM molecular weight generally tend to increase during storm episodes (Duan et al., 2007; Fellman et al., 2009; Hood et al., 2006; Inamdar et al., 2011; Li et al., 2005; Nguyen et al., 2013, 2010; Pellerin et al., 2012; Vidon et al., 2008), indicating a magnification of the terrigenous aromatic character of DOM, derived from shallow organic soils. Conversely, other parameters showed more unclear responses. For instance, the fluorescence index (FI, related to DOM sources) decreases (Inamdar et al., 2011; Vidon et al., 2008) or remains steady under high flows (Hood et al., 2006; Nguyen et al., 2013, 2010).

These studies originated from temperate and boreal streams and covered relatively short periods integrating a limited number of hydrological events (Austnes et al., 2010; Fellman et al., 2009; Hood et al., 2006; Inamdar et al., 2011; Nguyen et al., 2013, 2010; Spencer et al., 2010; Vidon et al., 2008). In contrast, research is still in the initial stage in intermittent streams that drain semi-arid or Mediterranean regions. Most of the on-going research specifically focus on the impact of drying-rewetting period on stream biogeochemistry (Fellman et al., 2011; Lake, 2011; Vázquez et al., 2011, 2007; von Schiller et al., 2015). However, intermittent streams are more complex than their well-known dry-wet cycle. Their hydrology shifts in a short time from unpredictable and intense storms to large, severe and predictable droughts. Consequently, it is possible to explore the plasticity of DOM quality under a large spectrum of hydrological conditions.

The specific aims of this study were:

1. describe the diversity of spectroscopic DOM properties under the widest range of hydrological conditions in an intermittent headwater stream and
2. investigate the potential legacy of antecedent hydrological, climatic and biogeochemical conditions on the variability of DOM-Q responses.

We hypothesised that discharge would modulate stream DOM properties and that this relationship would differ in contrasted hydrological periods. Moreover, we expected that the antecedent conditions of the storm events, such as the magnitude of the previous storm and the duration of the antecedent baseflow period, would affect the DOM-Q responses.

Here, we describe the results from an intensive, 2.5-year-long hydro-biogeochemical monitoring in a small, intermittent Mediterranean headwater stream. DOM was analysed in terms of carbon content (DOC) and spectroscopic properties (absorbance and fluorescence). The variability of responses of DOC and DOM qualitative descriptors with respect to discharge was explored at the hydrological seasonal scale and at the single storm event scale. Several hydrological, climatic and biogeochemical parameters were calculated for each storm event. The contribution of each significant driver that emerged in the most robust multiple linear regression model was assessed with a commonality analysis (Ray-Mukherjee et al., 2014).

2. Materials and methods

2.1. Study site and field monitoring strategy

Fuirosos is a headwater stream that drains a 15 km^2 granitic catchment in Catalonia, in the north-east of the Iberian Peninsula (Fig. 1; 41° 42′ N; 2° 34′ E; 50–700 m a.s.l.). The Fuirosos catchment is highly forested (90%) and mostly undisturbed, with the presence of some isolated agriculture fields. The predominant vegetation is cork oak (*Quercus suber*) and pine tree (*Pinus halepensis*). The riparian vegetation is dominated by plane tree (*Platanus hispanica*) and alder (*Alnus glutinosa*). The climate is Mediterranean, with mild winters (mean of 7 °C in January) and warm summers (mean of 23 °C in August). Annual precipitation ranges between 600 mm and 900 mm, with intense storms in spring and autumn and a severe summer drought (Ninyerola et al., 2000). The strong seasonality of the precipitation regime determines severe water-deficit stress and flow cessation in summer. Within this context, Fuirosos represents a typical semi-pristine intermittent stream with dry-wet cycles and it has become a reference site for fluvial ecology and biogeochemistry in the Mediterranean area (Vázquez et al., 2013).

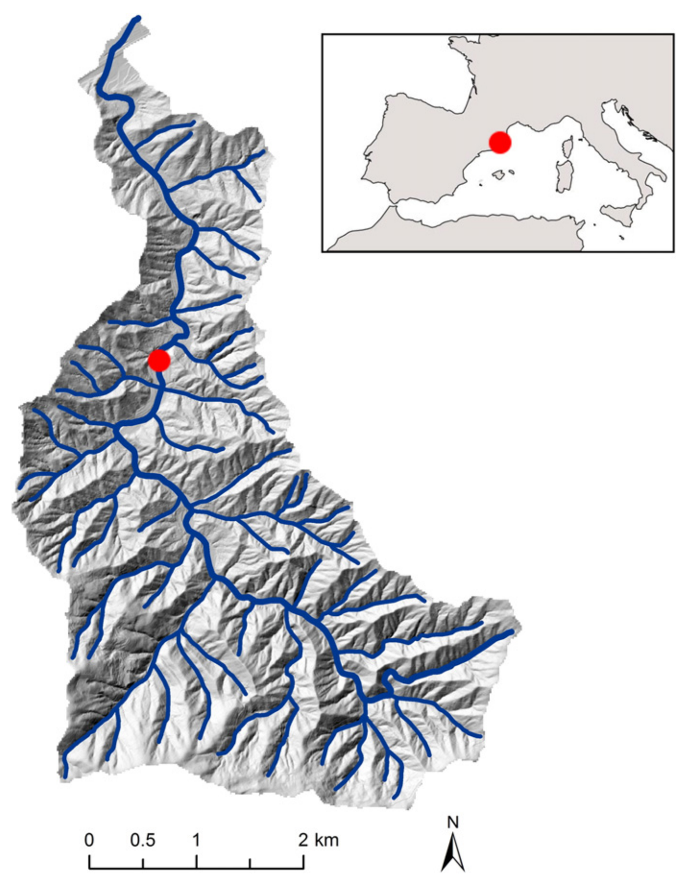

Fig. 1. Location of the sampling point in Fuirosos catchment. The hillshade is shown in grey colouring.

The riparian sediments are constituted by a gravel-sandy soil layer of 0.8–2.8 m thickness and a weathered granite layer of 2–11 m thickness. The groundwater level ranges from 0.5 m depth with respect to the ground surface in winter to 3.4 m depth in summer. The high hydraulic conductivity favours the stream water infiltration into the aquifer, with a maximum peak of specific discharge of 1.5 m^{-1} d^{-1}. The mixing area of the infiltrating stream water and the hillslope groundwater expands 3–10 m into the riparian area (Butturini et al., 2003).

The hydrological year in Fuirosos can be split into four sub-hydrological seasons (Bernal et al., 2005):

- The rewetting period. Typically in early fall (September–October), it describes the beginning of the hydrological year, with an abrupt and short hydrological transition from the total summer drought to the re-establishing of the normal water flow.
- The wet period. From late fall to late winter (November–February) with basal discharge typically higher than 5×10^{-3} m^3 s^{-1}.
- The vegetative period. From early spring to early summer (March–June) with basal flow of approximately 5×10^{-3} m^3 s^{-1}.
- The drying period. In early summer (June–July), runoff disappears in the tributaries and decreases rapidly from the main channel. During the rest of summer, the runoff vanishes from the entire system with the exception of a few disconnected pools (Vázquez et al., 2011).

A sub-daily-frequency hydro-biogeochemical programme was performed from May 2009 to December 2011. A stage actuated water sampler (Sigma 900 max) was used to collect a stream sample every 4–6 h. The samples were stored in the dark until they were collected. During storm periods, samples were brought to the lab every day. Under baseflow conditions, samples were collected manually every 4–7 days. Stream level was recorded every 30 min using a water pressure transducer connected to the automatic sampler. Discharge was estimated by mass balance calculation using the *slug* chloride addition method (Gordon et al., 2004). During the study, 47 hydrological high flow episodes occurred. The peak hydrographs were sampled in 72% of cases. The sampling captured the whole solute-discharge responses in 52% of the hydrological episodes. The wet and vegetative periods were the most represented, with 13 analysed storm events in each period. On the contrary, only 3 episodes from the drying period were captured.

2.2. Chemical and optical water analysis

Water samples were filtered with precombusted GF/F 0.7-μm filters (Whatman), acidified (pH = 2) and stored in the dark and cold (4 °C) until their analysis. DOM characterization was carried out using spectroscopic techniques. DOM optical properties can be related to biochemical characteristics and compositional changes of DOM with a minimum sample manipulation, high instrument sensitivity and rapid execution (Fellman et al., 2010). Nine DOM descriptors were estimated in this study: DOC concentration; 4 chromophoric indices — specific ultraviolet absorbance at 254 nm (SUVA), two intensity ratio of absorbances (E_2:E_3 and E_4:E_6) and spectral slopes ratio (S_R); and 4 fluorophoric indices — humification index (HIX), fluorescence index (FI), biological index (BIX) and the intensity ratio of two humic-like fluorescence peaks (A_C:C). These optical indices and the related biogeochemical interpretation are described in Table 1.

DOC was determined by oxidative combustion and infrared analysis using a Shimadzu TOC Analyser. Annual DOC export from the catchment was calculated by aggregating the daily fluxes obtained from the daily average values of discharge and DOC. Linear interpolation with time as the independent variable was performed on the days when data were not available. Samples for the optical analysis were filtered just before their analysis with 0.22-μm-pore nylon membranes to avoid any possible impurities, and they were analysed at room temperature. Chromophoric DOM was measured by using the absorbance spectrum from 200 to 800 nm with a UV–Visible spectrophotometer UV1700 Pharma Spec (Shimadzu) and a deionised water blank was subtracted from each sample. Fluorescence spectra were obtained with an RF-5301 PC spectrofluorometer (Shimadzu) and standardised according to the method of Goletz et al. (2011) using Mathematica (Wolfram Research) software.

Table 1
Optical indices analysed in this study, including the description of their calculation and their biogeochemical interpretation according to the referenced literature.

Index	Calculation	Interpretation
SUVA	The normalisation of UV absorbance at 254 nm by DOC concentration.	It indicates the DOM aromaticity (Weishaar et al., 2003).
E_2:E_3	The ratio of absorbances at 250 nm and 365 nm.	High values suggest a low average molecular size of DOM. (De Haan and De Boer, 1987).
E_4:E_6	The ratio of absorbances at 465 nm to 665 nm.	It was first found to be inversely related to aromaticity, but was later found to be more related to humification (Chen et al., 1977).
S_R	The ratio of the log transformed absorbance spectra slope at 275–295 nm to that estimated in the range of 350–400 nm (Helms et al., 2008).	High values indicate a high proportion of the DOM molecular fraction with low molecular weight.
HIX	The sum of the fluorescence intensities between 300 and 345 nm divided by the sum of the intensities between 300 and 345 nm and between 435 and 480 nm, for an excitation wavelength of 254 nm (Ohno, 2002).	Higher values indicate a greater degree of DOM humification. (Zsolnay et al., 1999).
FI	The ratio of emission intensities at 470 nm and 520 nm emitted at an excitation of 370 nm (Cory and McKnight, 2005).	It provides information about DOM sources; high values (≈1.8) suggest the prevalence of autochthonous DOM, and low values (≈1.3) suggest the prevalence of allochthonous DOM. (McKnight et al., 2001).
BIX	The ratio of the fluorescence intensity emitted at 380 nm, corresponding to the maximum of intensity of the β fluorophore, and that emitted at 430 nm, which corresponds to the maximum of the humic fraction at an excitation of 310 nm (Huguet et al., 2009).	The β fluorophore is typical of autochthonous recent DOM release (Parlanti et al., 2000). Therefore, high BIX values (>1) suggest the presence of autochthonous and fresh DOM, whereas BIX values of 0.6–0.7 indicate a low or nil DOM autochthonous production.
A_C:C	The fluorescence intensity maxima in the area of 230–250 nm excitation and 420–460 nm emission wavelengths (peak A_C) divided by that of the area of 330–370 nm excitation and 430–460 nm emission wavelengths (peak C) (Coble et al., 2014, 1990)	Peak A_C is related to fulvic acids, more soluble and slighter in molecular size (McDonald et al., 2004), while peak C is associated with humic acids (Chen et al., 2003).

2.3. Description of DOM-Q responses

The relationship between DOM descriptors and discharge was explored for the entire data set, for each hydrological season and at storm events intervals. During the study period, discharge changed up to six orders of magnitude. As a consequence, the discharge was log transformed. The slopes of the DOM vs. discharge relationships (dDOM/dQ, where DOM stands for DOC, SUVA, E_2:E_3, E_4:E_6, S_R, HIX, FI, BIX, and A_C:C) were considered significant at $p < 0.05$.

The response of DOM during storm episodes was quantified by calculating the relative change of each DOM descriptor (ΔC), comparing the value during the storm peak with that one obtained during the pre-event basal discharge conditions. ΔC ranged between −1 and 1. A negative ΔC value (ΔC < −0.1) indicated a decrease of the DOM parameter, whereas a positive ΔC indicated an increase (ΔC > 0.1). Chemostasis was assumed when −0.1 < ΔC < 0.1 (Butturini et al., 2008). This descriptor was estimated for 34 storm episodes (72% of storms occurred during the study period).

In those cases when the entire storm episode was exhaustively sampled, the information regarding the nonlinearity of DOM-Q response and its rotational pattern (ΔR) was estimated. ΔR ranged between −1 and 1. If ΔR > 0.1, the hysteresis showed a clockwise rotational pattern, meaning that the solute changes anticipated those of discharge. If ΔR < −0.1, the hysteresis showed a counter-clockwise rotational pattern. In this case, the solute variations delayed those of discharge. If −0.1 < ΔR < 0.1, this indicated that the DOM-Q loop showed an ambiguous or non-existent rotational pattern. In this study, this information was available for 25 storm episodes (52% of events occurred during the study period).

The methodological aspects of the calculation of ΔC and ΔR are described by Butturini et al. (2008). The ΔC and ΔR pairs were plotted in the ΔR vs ΔC unit plane. This plane synthesized the diversity continuum across the geometrical forms of DOM-Q responses (Butturini et al., 2008). The heterogeneity of the DOM-Q hysteresis of each DOM parameter (H) was defined as the proportion of area (%) of the convex envelope that contained all points with respect to the total area of the ΔR vs. ΔC diagram (see Appendix A).

2.4. Data analysis and model selection

In this study, 18 environmental, hydrological, climatic and biogeochemical parameters were used as potential predictors of the variability of ΔC and ΔR descriptors during the storm events (Tables 2 and 3). These parameters attempt to capture the seasonal hydro-climatic variability and the short and long term antecedent hydrological conditions.

Multiple linear regression and commonality analysis (CA) were used to explore the relationship between ΔC or ΔR (the dependent variables) and all the potential drivers. The variables that did not satisfy normality according to the Saphiro-Wilk test (Shapiro and Wilk, 1965) were log-transformed. All data were centred by subtracting the variable mean and scaled by dividing by the standard deviation. A detailed explanation of the data analysis can be found in the Appendix B.

CA was recently proposed to assess the predictor contribution in multiple linear regressions on ecological and environmental data (Ray-Mukherjee et al., 2014). CA decomposes regression R^2 into its unique and common effects (Mood, 1971, 1969; Newton and Spurrell, 1967). Unique effects (U) indicate how much variance is uniquely accounted for by a single predictor, while common effects (C) indicate how much variance is common to a predictor set. Therefore, CA determines the variance contributed by each predictor by accounting for unique and common effects. A negative common effect, together with a large unique effect and a low R^2, may indicate that the variable is a suppressor (Zientek and Thompson, 2006). Therefore, it removes irrelevant variance in another predictor and thus increases the predictive ability of that predictor (or set of predictors) and R^2 by its inclusion in a regression equation (Jobson, 1991). We applied CA to the model selected by multiple linear regression for each DOM property in order to weight the importance and role of the predictors.

All of the data analyses were conducted with R version 3.1.1 (R Core Team, 2014) using the "leaps" package (Lumley, 2009) and the "yhat" package (Nimon et al., 2013).

Table 2
Drivers included in the analysis of the variability of ΔC and ΔR descriptors. They are classified into three groups: storm event drivers (E), storm pre-event hydrological drivers (PEH) and storm pre-event biogeochemical drivers (PEB).

Driver	Description	Group
ΔQ	Magnitude of the event: the discharge difference between peak hydrograph and pre-event basal discharge	E
L_{rs}	Length of the rising limb: the lag time (hrs) between peak flow and basal discharge. It provides an idea of the flashiness of the storm episode	E
T_{min}	The minimal temperature of the day during the hydrological episode	E
Q_b	The pre-event basal discharge	PEH
Q_m	The average discharge during the month prior to the storm event	PEH
Δt_{-1}	Inter-storm time interval: the lag time between the storm and the preceding one	PEH
ΔQ_{-1}	Magnitude of the previous storm event: calculated as ΔQ	PEH
Δt_0	The time elapsed from the starting of the rewetting period	PEH
DOM_b	DOC, SUVA, S_R, E_2:E_3, E_4:E_6, FI, BIX, HIX and A_C:C values during the pre-event basal discharge	PEB
DOC_m	DOC concentration average during the month prior to the storm	PEB

3. Results

3.1. Hydrological variability and DOC fluxes

During the study period, Fuirosos surface flow stopped in June–July and recovered in September–October (Fig. 2). The basal discharge typically increased to an average value of 0.018 $m^3\ s^{-1}$ during the wet and vegetative periods. The magnitude of storm episodes (ΔQ) ranged widely from 0.005 $m^3\ s^{-1}$ to 22.789 $m^3\ s^{-1}$. The flashiness of the hydrographs also noticeably changed. The rising limb of the hydrograph (L_{rs}) was shorter than 12 h or 24 h in 51% and 72% of the events, respectively. The lag time between two consecutive rain episodes (Δt_{-1}) averaged 19 days. However, in summer, there were much longer periods without precipitation: 124 days in summer 2009, 77 days in summer 2010 and 89 days in summer 2011.

The annual DOC exports were 432 kg C $km^{-2}\ yr^{-2}$ and 697 kg C $km^{-2}\ yr^{-2}$ in 2009–2010 and 2010–2011, respectively. The vegetative period contributed up to 63–81% of the total annual flux, followed by the wet period (18–34%), the rewetting period (1–3%) and finally the drying period (0.2–0.3%). The 90–91% of the annual DOC export was flushed during storm events.

3.2. DOM-Q relationships

3.2.1. Seasonal variations

DOC and most of the DOM optical parameters were strongly related to discharge (Fig. 3; $10^{-66} < p < 10^{-11}$). The most discharge dependent parameters were DOC, BIX and FI ($0.326 < R^2 < 0.592$). SUVA, HIX and E4:E6 were also significantly related to discharge, however the explained variance decreased ($0.138 < R^2 < 0.18$). Finally, S_R, A_C:C and E_2:E_3 appeared nearly chemostatic with respect to discharge ($R^2 < 0.09$).

The hydrological period greatly influenced the slope and strength of the relationships between DOM descriptors and discharge (Fig. 4). The *d*DOM/*d*Q values of SUVA, FI, BIX and A_C:C changed gradually from the rewetting to the drying period. The most notable shifts were those of *d*FI/*d*Q (which changed from a highly negative slope to a positive slope) and *d*A_C:C/*d*Q (which changed the opposite way). The S_R parameter also reversed the sign of its slope during the drying. During the drying period, most of the *d*DOM/*d*Q slopes were not significant ($p > 0.1$). The exception was the E_2:E_3 descriptor, with the strongest relationship with discharge ($p < 10^{-4}$) during this period.

3.2.2. Storm to storm responses

The ΔC vs. ΔR unit plane synthesized the diversity of the DOM-Q loops at the storm event scale (Fig. 5, Table 4). The most homogenous DOM-Q loops were that of SUVA and DOC (H < 14%). Further, the convex envelopes of DOC, SUVA and E_4:E_6 nearly overlapped each other. Conversely, the most heterogeneous loops were that of E_2:E_3 and S_R.

Flushing responses during storm events predominated for DOC, SUVA, HIX and E_4:E_6. Dilution prevailed for E_2:E_3, S_R and BIX. Chemostasis (−0.1 < ΔC < 0.1) was the most frequent situation for A_C:C. Finally, both dilution and chemostasis were equally frequent for FI.

Table 3
Values of the potential drivers for each studied storm event: basal discharge (Q_b), magnitude (ΔQ), length of the rising limb (L_{rs}), minimal temperature of the day (T_{min}), number of days from the annual rewetting (Δt_0), time since the preceding storm event (Δt_{-1}), magnitude of the preceding storm event (ΔQ_{-1}), mean discharge of the preceding month (Q_m), mean DOC of the preceding month (DOC_m) and basal values of DOM properties (DOC_b, $SUVA_b$, E_2:E_{3b}, E_4:E_{6b}, SR_b, HIX_b, FI_b, BIX_b and A_C:C_b).

Date	Q_b (m^3 s^{-1})	ΔQ (m^3 s^{-1})	L_{rs} (h)	T_{min} (°C)	Δt_0 (d)	Δt_{-1} (d)	ΔQ_{-1} (m^3 s^{-1})	Q_m (L s^{-1})	DOC_m (mg L^{-1})	DOC_b (mg L^{-1})	$SUVA_b$ (L mg C^{-1} m^{-1})	E_2:E_{3b}	E_4:E_{6b}	S_{Rb}	HIX_b	FI_b	BIX_b	A_C:C_b
23/10/2009	0	0.016	2	10.0	1	124	0.002	0	3.7	3.9	4.4	5.8	4.0	0.86	0.93	1.67	0.59	1.80
22/12/2009	0.005	0.008	10	9.3	62	61	0.016	3	2.2	2.0	6.1	5.2	0.6	0.88	0.87	1.66	0.60	1.79
05/01/2010	0.009	0.006	11	7.9	63	11	0.005	6	2.2	2.2	6.9	4.2	3.0	0.82	0.92	1.66	0.59	1.79
07/01/2010	0.009	0.038	12	0.8	77	3	0.006	7	2.2	2.0	7.5	5.1	6.0	0.88	0.91	1.63	0.61	1.87
15/01/2010	0.024	0.026	28	2.3	84	7	0.038	16	2.7	2.6	6.8	5.6	4.0	0.83	0.93	1.62	0.60	1.96
09/02/2010	0.011	0.952	18	0.4	104	4	0.005	20	2.8	2.6	5.7	5.9	4.0	0.85	0.89	1.60	0.61	1.94
17/02/2010	0.021	0.059	32	−1.7	115	8	0.952	42	4.6	4.5	6.4	6.3	6.0	0.69	0.93	1.50	0.54	2.02
20/02/2010	0.052	0.456	30	5.5	120	3	0.059	44	4.9	4.3	6.4	5.6	2.5	0.77	0.93	1.49	0.54	1.97
05/03/2010	0.016	0.060	58	6.5	132	14	0.456	76	5.1	3.8	5.9	5.7	3.0	0.94	0.93	1.52	0.57	1.95
09/03/2010	0.051	0.258	46	1.5	137	4	0.060	82	5.1	3.6	6.9	5.1	2.3	0.93	0.94	1.50	0.55	1.91
15/03/2010	0.148	0.149	62	0.7	143	5	0.258	89	5.0	4.9	6.7	5.9	3.5	0.82	0.94	1.49	0.52	1.87
04/05/2010	0.007	2.756	36	13.3	188	22	0.007	16	3.0	2.8	5.5	5.9	4.0	0.88	0.86	1.54	0.57	1.98
14/05/2010	0.075	0.646	39	9.3	203	10	2.756	116	6.1	4.7	5.5	5.8	2.5	0.87	0.90	1.43	0.57	2.07
18/09/2010	0	0.472	6	12.6	1	50	0.005	0	4.0	3.7	7.3	6.4	3.2	0.77	0.92	1.78	0.61	1.76
24/09/2010	0.014	0.025	5	14.7	5	6	0.472	58	5.3	4.7	8.1	5.1	4.0	0.88	0.91	1.63	0.56	1.93
12/10/2010	0.004	3.852	59	16.3	23	18	0.025	46	5.9	3.7	7.4	6.0	8.0	0.81	0.91	1.68	0.58	1.80
13/10/2010	0.825	3.242	7	12.2	27	1	3.852	144	6.0	7.4	9.8	5.4	11.0	0.72	0.92	1.49	0.51	1.98
23/12/2010	0.015	0.216	59	−1.5	91	23	0.011	15	2.6	2.4	5.8	6.3	4.0	0.77	0.88	1.61	0.61	1.93
17/02/2011	0.016	0.009	7	2.8	154	19	0.099	28	2.2	2.5	6.5	5.6	3.0	0.85	0.90	1.54	0.55	1.88
03/03/2011	0.011	0.034	20	3.1	167	14	0.009	23	2.4	2.0	6.8	5.6	2.0	0.85	0.91	1.53	0.59	2.02
12/03/2011	0.021	5.770	16	6.1	177	9	0.035	20	2.3	2.2	6.5	5.5	3.0	0.88	0.90	1.54	0.58	1.96
15/03/2011	0.532	16.511	24	7.1	179	3	5.770	199	3.8	5.3	7.7	5.6	6.0	0.81	0.93	1.45	0.51	1.93
28/04/2011	0.015	0.014	4	7.7	224	5	0.123	24	2.7	2.9	5.8	5.4	3.0	0.84	0.87	1.51	0.56	1.99
01/06/2011	0.003	0.034	23	11.5	243	17	0.014	9	2.7	2.6	5.5	6.0	6.0	0.79	0.90	1.57	0.57	1.96
02/06/2011	0.020	0.024	8	7.6	259	1	0.034	9	3.2	2.7	6.3	5.9	3.0	0.77	0.91	1.53	0.56	1.99
05/06/2011	0.012	0.017	15	9.6	260	3	0.024	10	3.1	2.7	6.2	5.8	2.0	0.90	0.87	1.58	0.59	2.07
10/06/2011	0.020	0.041	11	10.8	267	5	0.017	13	3.1	2.9	5.7	5.8	4.0	0.79	0.86	1.53	0.57	2.03
15/07/2011	0.001	0.009	28	14.5	301	34	0.041	1	3.3	3.2	6.6	5.1	4.0	0.98	0.92	1.69	0.58	1.80
17/07/2011	0	0.013	10	12.9	302	3	0.009	1	3.6	3.5	7.0	4.8	6.0	0.89	0.92	1.74	0.59	1.71
26/07/2011	0.003	0.055	4	14.9	313	9	0.013	2	3.5	3.2	5.9	6.5	4.0	0.89	0.90	1.59	0.58	1.96
24/10/2011	0	0.071	3	9.6	1	89	0.007	0	3.5	3.7	6.1	5.4	6.0	0.69	0.89	1.66	0.61	1.87
28/10/2011	0.005	0.308	26	9.6	1	4	0.071	5	7.7	6.6	6.8	4.8	8.0	0.72	0.90	1.92	0.57	1.35
06/11/2011	0.016	1.424	60	12.7	8	9	0.308	27	6.3	4.3	6.8	3.4	5.0	0.72	0.90	1.67	0.57	1.83
15/11/2011	0.026	22.789	15	8.8	22	2	0.013	56	6.8	5.4	6.6	5.5	6.0	0.77	0.92	1.59	0.56	1.84

DOM-Q rotational patterns, ΔR, were highly heterogeneous. For instance, comprising all DOM descriptors, clockwise, no loop ($-0.1 < \Delta R < 0.1$) and counterclockwise hysteresis were the 29%, 36% and 35%, respectively. Clockwise loops predominated for SUVA and FI. Responses without a clear rotational pattern were more frequent for DOC and E_4:E_6. Counterclockwise loops emerged for E_2:E_3, S_R, BIX and A_C:C. Finally, for HIX the occurrence of ambiguous and counterclockwise responses was similar.

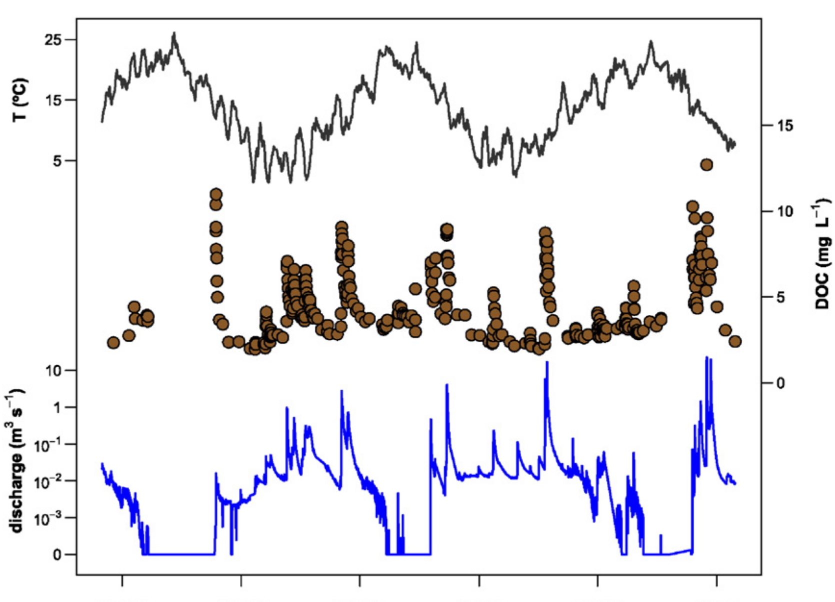

Fig. 2. Discharge (blue line), DOC (brown dots) and water temperature (grey line) during the study period in Fuirosos stream.

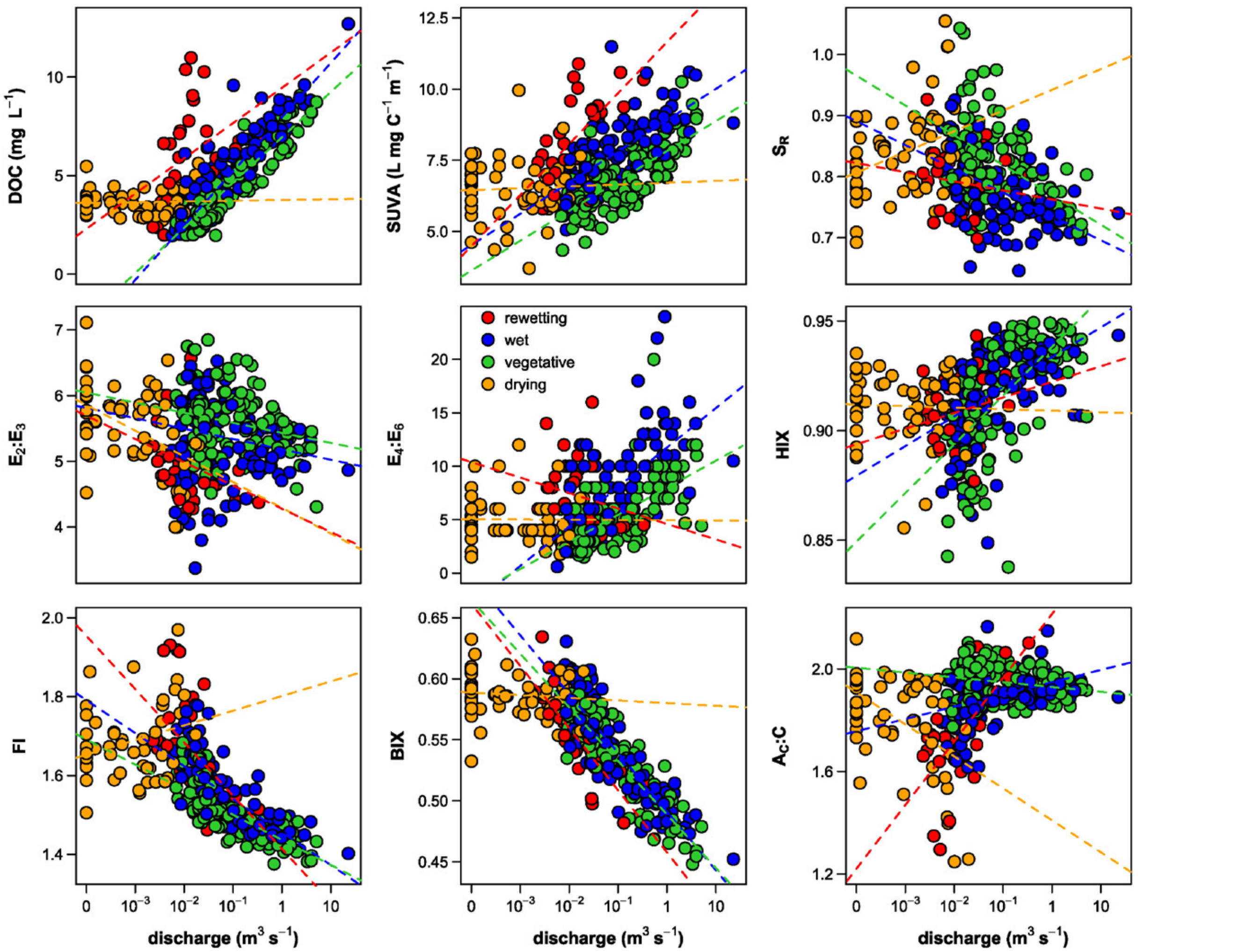

Fig. 3. Relationships between DOM descriptors and discharge during the study period. Dashed lines show the slope of the DOM descriptor vs. discharge linear relationship for each hydrological period. Significance levels are described in Fig. 4.

Clear differences in DOM-Q loops across hydrological periods were not observed. However, the most anomalous DOM-Q loops were typically monitored during rewetting (DOC, SUVA and E_2:E_3) and drying (S_R, FI and A_C:C) periods. BIX was the only DOM descriptor that showed a separation between hydrological periods, with rather clockwise loops in the wet period and counterclockwise loops in the vegetative period.

3.3. Drivers of ΔC and ΔR descriptors

ΔC was significantly related ($p < 0.05$) to the magnitude of storm events (ΔQ) for most DOM descriptors, namely DOC ($R^2 = 0.500$), SUVA ($R^2 = 0.194$), E_4:E_6 ($R^2 = 0.153$), FI ($R^2 = 0.296$) and BIX ($R^2 = 0.459$). In those cases, we set the residuals ($\Delta C_{(r)}$) of the ΔC vs. ΔQ regression as the dependent variables of the multiple regression. Table 5 summarizes the results of CA for each ΔC or $\Delta C_{(r)}$, after the selection of the optimal multiple regression model. Five models explained >75% of the variance. The drivers more frequently selected were Δt_{-1} and Δt_0 (in 5 models) and Q_b (4 models).

In most of the selected models, DOM biogeochemical status during the pre-event baseflow was a relevant driver, showing a negative relationship with ΔC. The model for ΔC_{HIX} explained 81.8% of the variance with only 4 drivers, with HIX_b as the most important. Regarding $\Delta C_{E2:E3}$, the most relevant drivers were $E2:E3_b$ and Δt_{-1}. BIX_b explained 48.1% of the variance in $\Delta C_{BIX(r)}$, while 7 other drivers explained a little fraction each one. In this model Δt_0 showed relatively high unique effects and high negative common effects ($C = -0.136$), and, therefore, although it had low total effects, it acted as a suppressor driver. The model for ΔC_{SR} selected only 2 drivers, the most relevant was S_{Rb} explaining 41% of the variance. Finally, the model for $\Delta C_{E4:E6(r)}$ had a poor performance (10% of the variance explained), and E_2:E_{3b} (negative relationship) was the single driver selected.

Δt_0 was the main driver for $\Delta C_{AC:C}$ and $\Delta C_{FI(r)}$ and showed a positive relationship with them. The model for $\Delta C_{AC:C}$ included 8 drivers, and Δt_{-1} acted as a suppressor ($C = -0.390$). The model selected for $\Delta C_{FI(r)}$ integrated also 8 drivers and Q_b ($C = -0.307$) and L_{rs} ($C = -0.317$) acted as suppressors.

Short time antecedent hydrological conditions were important drivers for some DOM descriptors. For $\Delta C_{DOC(r)}$ the selected model explained 65% of its variance and ΔQ_{-1} was the most relevant driver. With respect to $\Delta C_{SUVA(r)}$, the selected model included three drivers and explained 49% of the total variance. Q_b showed the higher total effects in this case. Both parameters were inversely related to the respective ΔC.

The models selected to explain the variability of ΔR_{DOM} descriptors (Table 6) were less robust than those selected for ΔC_{DOM}. The ΔR_{BIX} model was not significant ($p > 0.05$). The models with the highest explained variance were those selected for ΔR_{FI} and ΔR_{SUVA}. In the former, the most important predictor was ΔQ (52.3% of the variance explained), while in the latter it was S_{Rb} (15.8%). The drivers more frequently selected among the 9 models were Δt_0 and BIX_b (in 5 models) and DOC_b (4 models).

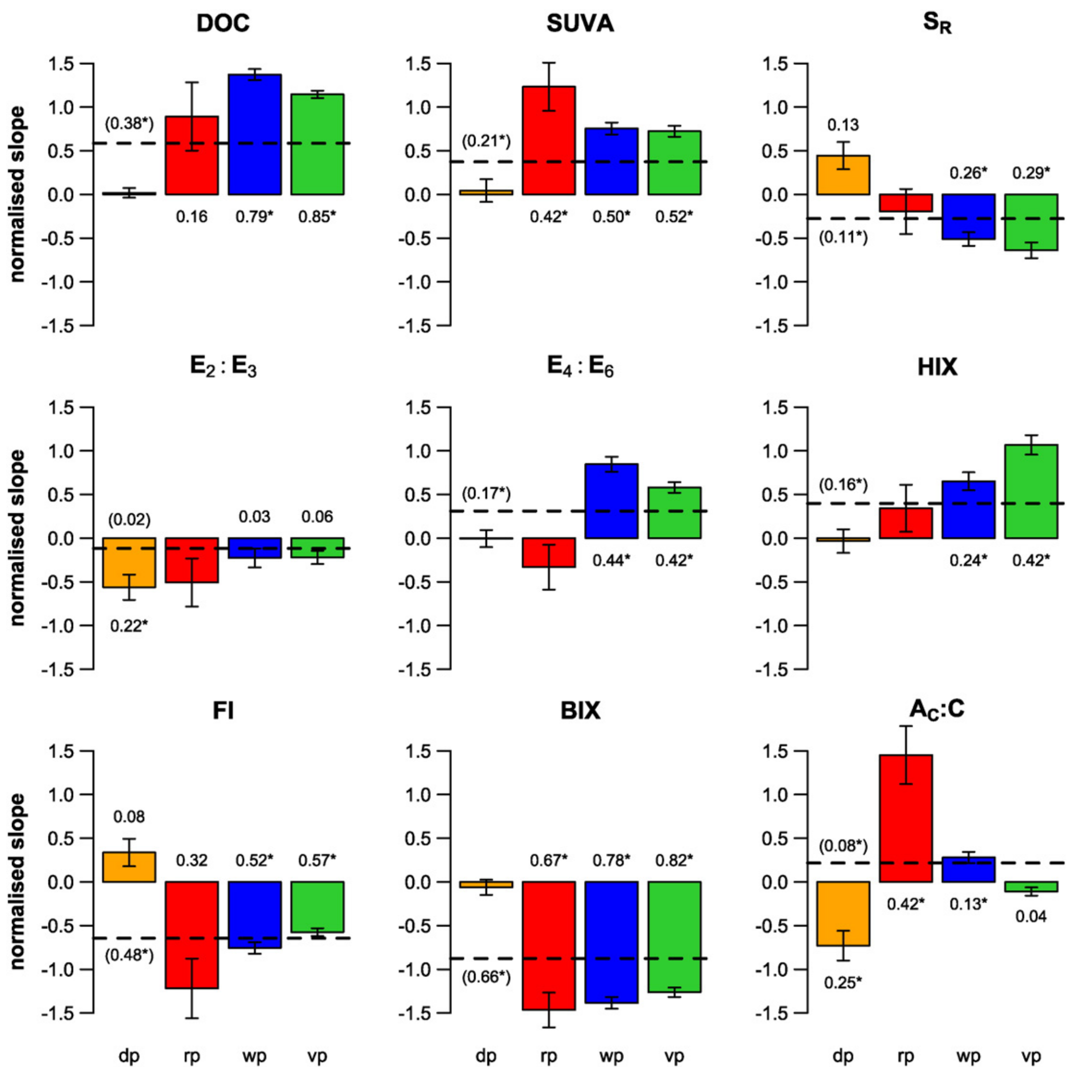

Fig. 4. Slopes of the linear regression relating the normalized DOM descriptors with the logarithm of discharge in the different hydrological periods (dp = drying, rp = rewetting, wp = wet, vp = vegetative). Error bars indicate ±1 standard error of the slopes. Dashed lines represent the slope of the entire data set. R^2 for each regression is shown when $p < 0.05$ (in parenthesis accounting for the data altogether); * indicates that $p < 0.001$.

4. Discussion

4.1. DOM-Q relationships

This study revealed how a complex coupling of hydrological, climatic and biogeochemical factors modulated the variability of the DOM concentration and quality in a headwater intermittent stream. These factors interacted with each other and interfered with the DOM dynamic at annual, seasonal and storm event scales.

To date, hysteresis approach focuses on sediment transport (Ziegler et al., 2014), nutrients (Bowes et al., 2015; Darwiche-Criado et al., 2015) and DOC (Butturini et al., 2008, 2006). The present study is, as far as we know, the first attempt to describe shifts of DOM quality under a large spectrum of hydrological conditions in a Mediterranean headwater stream, and to relate these shifts to environmental drivers. A previous study performed in Fuirosos during four years did not identify any predictable pattern of DOC-Q responses (Butturini et al., 2008). Consequently, the analysis of predictability of DOM-Q hysteresis is a challenging task. Moreover, the hydro-climatic characteristics in the Mediterranean region are being altered (Barrera-Escoda and Llasat, 2015; Vicente-Serrano et al., 2014). Therefore, it is crucial to assess how magnitude and frequency of storm events and severity of drought episodes influence on DOM quantity and quality in headwater streams.

Most of the DOM was flushed downstream under high flow conditions. This circumstance had enormous biogeochemical implications because over an entire year, a large proportion of DOM moved rapidly downstream with little chance to be processed by the system. However, these DOM pulses would be essential carbon and energy input sources for heterotrophic microbiota in downriver alluvial floodplains or even in the coastal system (McLaughlin and Kaplan, 2013; Palmer et al., 2015).

DOM in Fuirosos is commonly terrigenous, aromatic, degraded, humic and with high molecular weight, but it strongly exacerbates these properties at high flows. These changes reflected modifications in flow paths during rain episodes (Hinton et al., 1998), with subsequent DOM mobilization from near surface organic rich soil, via overland flow or preferential flow through soil macropores (Vidon et al., 2008). Thus, DOM concentration and properties were greatly chemodynamic with respect to discharge. These results coincided with that reported in most of the forested headwaters located in boreal, temperate and alpine systems (Buffam et al., 2001; Li et al., 2005; Hood et al., 2006; Vidon et al., 2008; Fellman et al., 2009; Saraceno et al., 2009; Nguyen et al., 2010; Spencer et al., 2010; Inamdar et al., 2011; Nguyen et al., 2013; Singh et al., 2015; Fasching et al., 2016). These consistencies in the DOM-discharge relationship worldwide marked the bond between discharge and DOM concentration and quality.

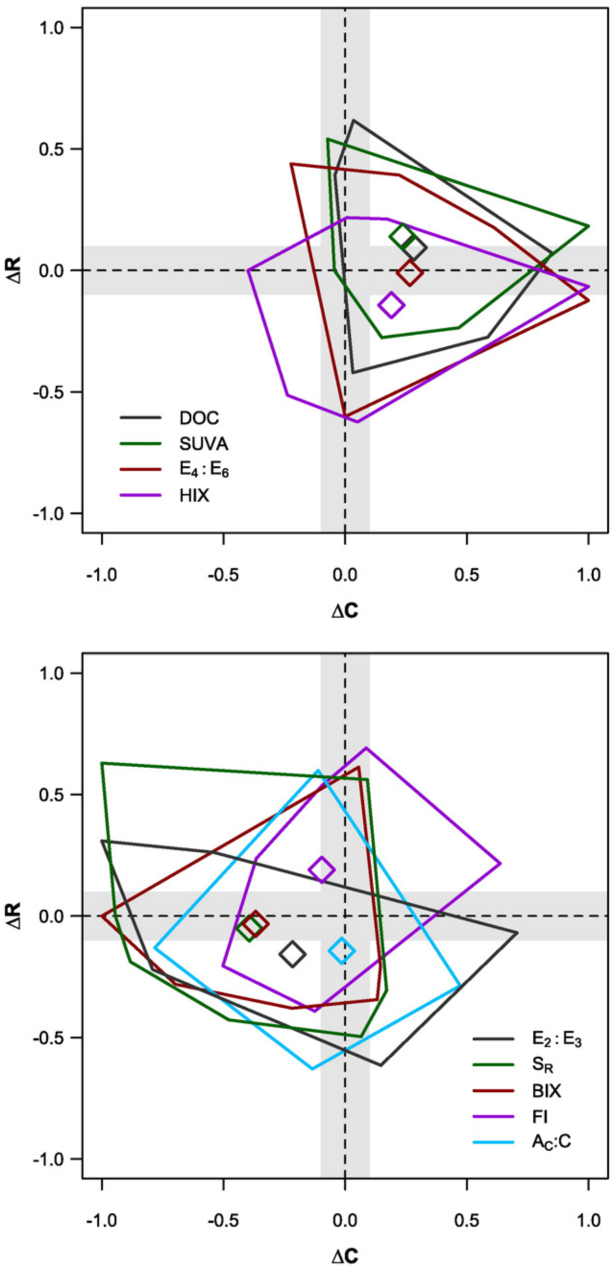

Fig. 5. Convex envelopes and mean (rhombus) for each DOM descriptor in the ΔR vs. ΔC unit plane.

4.2. Seasonal patterns: drying and rewetting

Sensitivity to discharge strongly varied across hydrological seasons. Thus, for most of the DOM descriptors, the connection with discharge vanished or reversed during the drying phase. In Fuirosos, this period implicated a rapid reduction of water flow, large water residence times and the fragmentation of the river continuum (Vázquez et al., 2011). A slight increase of FI and BIX might reflect a moderate increase of the contribution of autochthonous DOM during this phase. E_2:E_3 also increased as drying advanced, a pattern that revealed the decrease of the average DOM molecular weight. Von Schiller et al. (2015) attributed this trend to the decline in the proportion of large sized polysaccharides, probably due to their bioavailability as a source of DOM for microbial heterotrophs (Ylla et al., 2010).

The rewetting period represented a drastic change in the hydro-biogeochemical conditions. In few hours, the riparian groundwater was recharged by stream water, and the solute exchange across the stream-riparian interface was restored (Butturini et al., 2003; Vázquez et al., 2007). The abrupt hydrological reconnection between forest hillslopes and stream channel, and the water-solute exchange across the stream-riparian interface, reactivated the DOM vs. discharge relationship for most of the DOM descriptors and promoted the largest dDOM/dQ slope values for SUVA, A_C:C, BIX and FI. Therefore, high discharges during the rewetting period leaded to a disproportionate input of allochthonous, degraded and aromatic DOM. Among these parameters, the most remarkable response was that of the A_C:C. High values of A_C:C have been associated with photobleaching or microbial degradation of terrestrially derived DOM (Hur and Cho, 2012; Zhang et al., 2011). The Fuirosos fluvial channel is mostly shadowed by a dense riparian strip. Consequently, the anomalous fulvic-like substances peak might reflect the accumulation of these substances in the stream bed during the drought period.

4.3. DOM-Q hysteresis heterogeneity

Although the analysis of hysteresis loops in fluvial hydro-biogeochemistry was proposed in the 1970s and 1980s (Johnson and East, 1982; Walling and Foster, 1975; Williams, 1989), this approach is becoming a growing research topic after Evans and Davies (1998) and House and Warwick (1998) and is providing new advances into hydrological and biogeochemical functioning in rivers (Butturini et al., 2008; Fovet et al., 2015; Lloyd et al., 2016; Zuecco et al., 2015). Overall, DOM-Q hysteresis in Fuirosos were highly heterogeneous. However, within this high variability, some patterns emerged. Thus, the predominance of clockwise loops of SUVA and FI and the predominance of counterclockwise loops of E2:E3, S_R and A_C:C suggested a rapid mobilization of poorly degraded, large size and aromatic DOM pool from a near-stream source (Lloyd et al., 2016), such as a river bed, hyporheic or riparian zones (Butturini et al., 2006). Conversely, the input of more

Table 4
Distribution of DOM-Q loops types according the ΔC and ΔR descriptors for each DOM property, expressed in % of the studied cases. ΔC and ΔR were estimated for 34 and 25 storm episodes respectively. The last column describes the heterogeneity of DOM-Q loops responses (H).

DOM descriptor	ΔC			ΔR			H (%)
	Dilution	Chemostasis	Flushing	Counter-clockwise	No loop	Clockwise	
	ΔC < −0.1	−0.1 < ΔC < 0.1	ΔC > 0.1	ΔR < −0.1	−0.1 < ΔR < 0.1	ΔR > 0.1	
DOC	0	41	59	12	52	36	13.5
SUVA	0	29	71	8	24	68	12.5
E_2:E_3	59	29	12	60	28	12	20.8
E_4:E_6	9	24	68	32	40	28	17.3
S_R	65	15	21	48	32	20	26.8
FI	44	44	12	8	36	56	16.3
HIX	12	41	47	44	48	8	16.8
BIX	74	15	12	44	36	20	16.8
A_C:C	29	53	18	56	32	12	19.3

Table 5
Total effects and unique effects (in parenthesis) obtained in the commonality analysis of each ΔC descriptor. The subindex (r) indicates that the residuals from the ΔC–ΔQ relationship are used as the dependent variable (see Appendix B). A positive sign before a total effect value indicates a positive relationship between the driver and the ΔC; a negative sign indicates an inverse relationship. The higher value of each ΔC descriptor is in bold. The statistics of the multiple linear regressions are also shown. NS indicates a non-significant relationship ($p > 0.05$).

	Dependent variables								
Indep. variables	$\Delta C_{DOC(r)}$	$\Delta C_{SUVA(r)}$	$\Delta C_{E4:E6(r)}$	$\Delta C_{FI(r)}$	$\Delta C_{BIX(r)}$	$\Delta C_{E2:E3}$	ΔC_{SR}	ΔC_{HIX}	$\Delta C_{AC:C}$
ΔQ	Removed	Removed	Removed	Removed	Removed	−0.008 (0.036)	−0.051 (0.159)		
L_{rs}				−0.045 (0.362)				+0.168 (0.228)	+0.077 (0.284)
T_{min}	+0.051 (0.074)					−0.030 (0.055)		−0.019 (0.031)	
Q_b		**−0.308** (0.075)		+0.055 (0.362)	+0.163 (0.063)				−0.002 (0.310)
Q_m								−0.069 (0.037)	
Δt_{-1}				+0.006 (0.308)	+0.128 (0.088)	−0.221 (0.037)		−0.018 (0.059)	−0.044 (0.434)
ΔQ_{-1}	**−0.394** (0.136)			−0.049 (0.072)					+0.001 (0.084)
Δt_0	−0.049 (0.118)	−0.067 (0.084)		**+0.179** **(0.432)**	+0.060 **(0.195)**				**−0.210** **(0.480)**
DOC_m						+0.034 (0.061)			
DOC_b				+0.022 (0.240)					−0.008 (0.172)
$SUVA_b$	−0.278 **(0.167)**	−0.251 **(0.160)**			+0.204 (0.028)				
$E_2{:}E_{3b}$			**−0.101**			**−0.467** **(0.486)**			
$E_4{:}E_{6b}$									
S_{Rb}					−0.016 (0.032)		**−0.256** **(0.364)**		
HIX_b				+0.023 (0.163)	+0.166 (0.079)			**−0.445** **(0.646)**	
FI_b					+0.070 (0.072)				−0.019 (0.156)
BIX_b				+0.085 (0.063)	**−0.481** (0.120)				
$A_C{:}C_b$						+0.006 (0.113)			−0.058 (0.127)
Statistics									
p-value	$<10^{-5}$	$<10^{-3}$	NS	$<10^{-5}$	$<10^{-5}$	$<10^{-7}$	$<10^{-3}$	$<10^{-8}$	$<10^{-5}$
R^2	0.652	0.491	0.100	0.779	0.803	0.809	0.414	0.818	0.798
BIC	80.7	90.2	102.4	79.4	79	67.4	91.4	62.1	79.8

allochthonous and highly degraded DOM appeared more linked to a slower input from shallow soil and groundwater (Inamdar et al., 2013).

DOM-Q hysteresis showed an important heterogeneity in the ΔR vs. ΔC plane, and a typical response did not exist. Their variability, with the exception of BIX variability, did not exhibit any seasonal pattern. Strohmeier et al. (2013) reported a clear counterclockwise response of DOC concentration in a forested catchment, with larger hysteresis in summer and fall. Our study covered 2.5 years, probably a temporal interval too short to discern consistent seasonal patterns. Storm events that occurred during the most short and abrupt periods (drying and rewetting periods) represent a relatively small fraction of the total sampled events (9% and 15%, respectively). Therefore, to have a more consistent opportunity to discern seasonality of DOM-Q loops, it is essential to incorporate more cases of these critical periods. This implicates to generate larger hydro-biogeochemical temporal series.

4.4. Drivers of ΔC and ΔR variability

Storm magnitude (ΔQ) emerged as an essential driver for ΔC variability. This is an expected result because the strong link between DOM and discharge is well known in headwater streams (Nguyen et al., 2013). However, ΔQ, with the exception of FI, did not emerge as a significant driver of DOM-Q hysteresis shape and rotational patterns (ΔR).

More interestingly, several pre-event drivers significantly influenced both the magnitude of DOM responses and the timing of the flushing/dilution responses. Thus, Δt_0 significantly explained the variability of ΔC and ΔR in many models. This result showed that the impact of a drought period on DOM properties variability could extend up to the successive drying phase. Basal discharge (Q_b) significantly drove the variability of some models and resulted to be the most relevant driver for $\Delta C_{SUVA(r)}$, suggesting that Q_b shaped the flushing of DOM aromatic substances, with larger SUVA changes during storms preceded by low Q_b values. The magnitude of the antecedent storm episode (ΔQ_{-1}) was selected only in few models. However, it was the stronger driver for $\Delta C_{DOC(r)}$. Consequently, DOC flushing was amplified by the magnitude of the storm (ΔQ) but, at the same time, partially neutralized by the magnitude of the antecedent storm episode (ΔQ_{-1}). This flushing "memory" was similar to that reported in a boreal catchment, where the effect of a high export during the previous summer and autumn was still detectable during the following snowmelt (Ågren et al., 2010). However, the flushing memory reported in our study acted at storm-to-storm interval rather than at seasonal interval. The inter-storm time interval (Δt_{-1}) was selected in some models for ΔC. Larger Δt_{-1} intervals should promote a larger DOM flushing. However, this potential driver never emerged as the most relevant one, indicating that Δt_{-1} played a more subtle and diffuse role. Thus, a synergistic effect on DOC flushing between Δt_{-1} and ΔQ_{-1} did not appear, but it emerged between ΔQ_{-1} and Δt_0.

Pre-event basal biogeochemical conditions were frequently selected in the models, and they were the most significant drivers in several of them. Consequently, the pre-storm biogeochemical status needs to be considered when studying the variability of ΔC and ΔR descriptors

Table 6
Total effects and unique effects (in parenthesis) obtained in the commonality analysis of each ΔR descriptor. The higher value of each ΔR descriptor is in bold. A positive sign before a total effect value indicates a positive relationship between the driver and the ΔR; a negative sign indicates an inverse relationship. The statistics of the multiple linear regressions are also shown. NS indicates a non-significant relationship ($p > 0.05$).

Indep. variables	Dependent variables								
	ΔR_{DOC}	ΔR_{SUVA}	$\Delta R_{E2:E3}$	$\Delta R_{E4:E6}$	ΔR_{SR}	ΔR_{HIX}	ΔR_{FI}	ΔR_{BIX}	$\Delta R_{AC:C}$
ΔQ	−0.099 (0.087)			−0.016 (0.071)			**−0.523** **(0.456)**		
L_{rs}			+0.014 (0.125)	+0.065 (0.225)					
T_{min}			+0.079 (0.177)	+0.007 (0.154)			+0.025 (0.041)		
Q_b		+0.014 (0.167)		+0.009 (0.313)					+0.010 (0.085)
Q_m		−0.009 (0.123)		−0.038 **(0.346)**					
Δt_{-1}		+0.017 (0.122)							
ΔQ_{-1}							−0.140 (0.056)		−0.009 (0.250)
Δt_0	**+0.273** **(0.444)**	+0.144 (0.056)	**−0.243** (0.242)				−0.022 (0.057)		−0.099 (0.069)
DOC_m		+0.022 (0.096)	−0.010 (0.276)		−0.026 (0.064)				
DOC_b		−0.025 (0.134)	+0.017 **(0.297)**		+0.024 (0.166)				+0.170 **(0.274)**
$SUVA_b$						**−0.168** **(0.287)**			
$E_2{:}E_{3b}$				+0.024 (0.073)				**−0.125**	
$E_4{:}E_{6b}$		+0.002 (0.224)							
S_{Rb}	−0.011 (0.243)	**+0.158** (0.113)			+0.155 (0.188)				
HIX_b					**+0.177** (0.117)				**+0.191** (0.089)
FI_b									
BIX_b			+0.086 (0.222)	**+0.094** (0.061)	+0.019 **(0.272)**	−0.047 (0.166)	+0.208 (0.038)		
$A_C{:}C_b$	−0.011 (0.066)	−0.035 **(0.228)**							+0.025 (0.236)
Statistics									
p-value	$<10^{-3}$	$<10^{-2}$	$<10^{-3}$	$<10^{-2}$	10^{-2}	<0.05	$<10^{-5}$	NS	10^{-2}
R^2	0.632	0.792	0.726	0.638	0.625	0.334	0.836	0.125	0.667
BIC	64	69	66	74	71	73	50	76	68

during storm episodes. On the contrary, more seasonal climatic related drivers, such as temperature during storms (Tmin) and average discharge during the month prior to the storm event (Qm), were selected sporadically, suggesting that climatic seasonality appeared unimportant.

It is necessary to note that most of the models that fitted ΔR variability were weaker than those selected for ΔC. As a consequence, some care is necessary in their interpretation. The estimation of ΔR is by far much more exigent than that of the ΔC because it depends on an exhaustive biogeochemical sampling during a whole storm episode. In this study, ΔR was estimated in only 52% of the observed storm episodes. Therefore, to advance in this direction, it is essential to minimise the gaps in the biogeochemical sampling programme and to increase the sampling frequency.

In the next future, the progressive improvement of large and high frequency DOM temporal series would stimulate the cross comparison of DOM temporal series worldwide. This step will be essential to have a full perspective of DOM quantitative and qualitative flushing responses and, at the same time, to capture the most relevant drivers for DOM dynamic under different climate types, flow regimes, groundwater contributions and land cover.

4.5. Conclusions

High flow conditions are crucial for DOM quantity and properties and the carbon cycle in headwater streams. However, little is known about the relevance of other environmental parameters; whether or not there is a synergy among them or with hydrology. At a storm event scale, DOM–Q responses were highly heterogeneous in a small, intermittent Mediterranean stream, and antecedent hydrological and biogeochemical conditions coupled to storm magnitude appeared to be important drivers for DOM–Q responses. During a short time interval, DOC flushing was partially inhibited by the magnitude of the previous storm episode (ΔQ_{-1}), and aromatic DOM flushing was more marked under pre-event low basal flow conditions (Q_b). With regards to larger time interval, the time elapsed from the previous summer drought (Δt_0) modulated the origin of DOM flushed during storms, from an accentuated allochthonous source during rewetting to slightly more autochthonous sources during the successive drying. These findings outline the importance of the memory effect on DOM. Therefore, under the threat of a change in frequency and magnitude of storm and drought episodes in Mediterranean catchments (Barrera-Escoda and Llasat, 2015; Vicente-Serrano et al., 2014), it will be necessary to generate larger pluri-annual high-frequency DOM temporal series to determine the possibility of an impact of an accumulative effect of concatenation of severe drought episodes on long-term DOM flux and fate.

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2016.07.060.

Acknowledgements

This research was funded by the Spanish Ministry of Education and Science (MEC) (CGL2011-30151-C02 and CGL2014-5876-C3-R) and the European Community 7th Framework Programme (No. 603629-

ENV-2013-6.2.1 GLOBAQUA). AG holds a predoctoral grant from the University of Barcelona. AB and AG are members of the research group FORESTREAM (2014SGR949). Authors thank Elisabet Ejarque-Gonzalez, M. Ángeles Gallegos and Dijana Grgas for field and laboratory assistance and three anonymous reviewers for their useful suggestions.

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